

CLAIMS

1. Porous membranes of (per)fluorinated amorphous polymers having a porosity in the range 5-500 nm, preferably 20-100 nm, determined by an atomic force electronic microscope.
2. Porous membranes of (per)fluorinated amorphous polymers according to claim 1, wherein the membrane pore average size distribution is narrow, about the 80%-90% of the pores having a size ranging from minus 5 nm to plus 5 nm of the value of the distribution maximum peak.
3. Porous membranes of (per)fluorinated amorphous polymers according to ^{claim 1} ~~claims 1-2~~ obtainable from the polymerization:

A) polymers of one or more monomers having structure

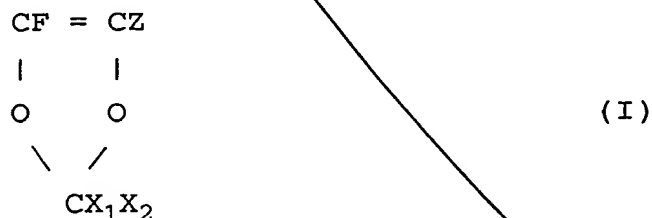
(II):



wherein: Y_1 and Y_2 are selected from F, Cl, CF_3 , OR_f

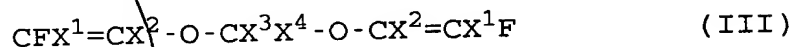
wherein R_f is a $\text{C}_1\text{-C}_5$ perfluoroalkyl radical;

with one or more comonomers having the following structures:



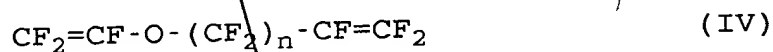
wherein: Z is selected from F, R_f, OR_f, preferably OR_f; R_f is a perfluoroalkyl radical C₁-C₅; X₁ and X₂ are selected from F and CF₃;

bisvinylloxymethanes having structure (III):



wherein X¹ and X², equal to or different from each other, are F, Cl, preferably F; X³ and X⁴, equal to or different from each other, are F or CF₃;

dienes having structure (IV):



wherein n = 1-5, preferably 1-2;

or

- B) homopolymers of monomers having structure (I) or (III) or (IV);
- C) copolymers of monomers having structure (I) or (III) or (IV).

4. Porous membranes of (per)fluorinated amorphous polymers according to claim 3, wherein the copolymer is derived from the structures (I) and (II) wherein Z=OR_f with R_f=CF₃, X₁, X₂, Y₁, Y₂=F.

5. Porous membranes of (per)fluorinated amorphous polymers according to ~~claim 3~~ ^{claim 3} ~~claims 3-4~~, wherein the dioxole percentage having structure (I) is in the range 40%-90% by moles, preferably 50%-85% by moles.

6. Porous membranes of (per)fluorinated amorphous polymers according to ^{claim 3} ~~claims 3-5~~, wherein as dioxole having structure (I) 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) is used. HE

5/23/64 7. Porous membranes of (per)fluorinated amorphous polymers according to ^{claim 3} ~~claims 3-6~~, wherein the monomers having structure (II) are selected from tetrafluoroethylene, perfluoroalkylvinylethers (C₁-C₅), hexafluoropropene, chlorotrifluoroethylene, tetrafluoroethylene (TFE) is preferably used.

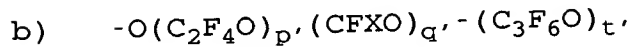
Mika 8. Process for obtaining the porous membranes of (per)fluorinated amorphous polymers according to ^{claim 1} ~~claims 1-7~~, comprising:

- the preparation at room temperature, in the range 15°C-25°C, of a solution of the amorphous polymer in a fluorinated solvent; the solution viscosity at 23°C being in the range 5-5.000 cP (centipoise), preferably 10-300 cP;
- the solution is spread on an inert support, preferably by a stratifying knife having a defined thickness;
- it is let evaporate at a constant temperature, preferably equal to that of the spreading, inferior of 10°C-45°C with respect to the solvent boiling temperature,

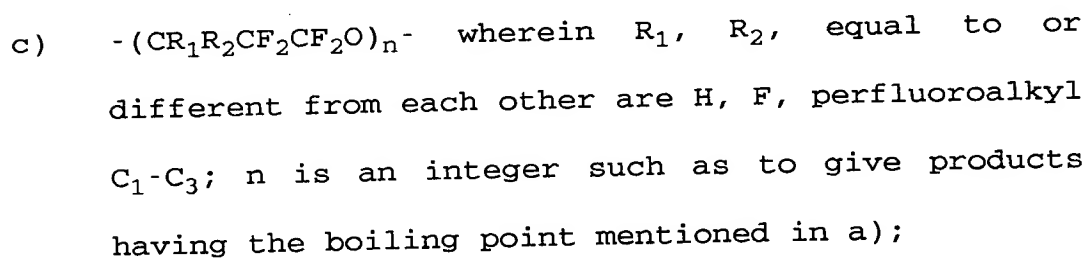
preferably inferior of 15°C-35°C, for such a time as to allow a slow evaporation of the solvent and the consequent formation inside the film of pores having the above mentioned sizes; said time being in the range from about 1 to 10 days, preferably 3-6 days.

9. A process according to claim 8, wherein the fluorinated solvent has preferably a boiling temperature in the range 50°C-300°C, preferably 50°C-150°C.
- ~ 10. A process according to ^{claim 8} ~~claims 8-9~~, wherein the polymer concentration in the solution is in the range 1-20% by weight, preferably 1-10% by weight.
- ~ 11. A process according to ^{claim 8} ~~claims 8-10~~, wherein the fluorinated solvent is selected from (per)fluoropolyethers (Galden®, Fomblin®, Krytox®, Demnum®), hydrofluoropolyethers (H-Galden®), fluorinated and perfluorinated ethers Fluorinert® (series FC and HFE) optionally containing one or more hydrogen atoms in the end groups, perfluoroalkanes.
- ~ 12. A process according to ^{claim 8} ~~claims 8-11~~, wherein the fluorinated solvent is selected from (per)fluoropolyethers containing the following units:
 - a) $-O(C_3F_6O)_m(CFXO)_n-$ wherein the units (C_3F_6O) and $(CFXO)$ are perfluorooxyalkylene units statistically distributed along the chain; m' and n' are integers such as to give products having boiling point gene-

rally in the range 60°C-300°C, preferably 60°C-150°C, and m'/n' is in the range 5-40, when n' is different from 0; X is equal to F or CF_3 ; n' can also be 0;



wherein p' , q' and t' are integers such as to give products having the boiling point mentioned in a), p'/q' ranges from 5 to 0.3, preferably from 2.7 to 0.5; t' can be 0 and $q'/(q'+p'+t')$ lower than or equal to 1/10 and the t'/p' ratio is from 0.2 to 6;



the end groups are selected from $-CF_3$, $-C_2F_5$, $-C_3F_7$, optionally containing one or two chlorine atoms, $-CF_2H$, $-CFHCF_3$.

13. A process according to claim 12, wherein the fluorinated solvent is dihydrofluoropolyether of type b) wherein t' is equal to 0, $X=F$ or CF_3 and both end groups are $-CF_2H$; the boiling point being in the range 50°C-80°C.

14. A process according to ^{claim 8} ~~claims 8-13~~, wherein the polymeric solution spreading and the solvent evaporation are carried out at a temperature between 10°C and 40°C and using

a fluorinated solvent having a boiling temperature between 55°C and 60°C.

15. A process according to ^{claim 8} ~~claims 8-14~~, wherein the support for the spreading of the polymeric film is selected from: glass/quartz, polymethylmethacrylate, polycarbonate, polyurethane, polystyrene, ceramic and metal supports, thermoplastic fluoropolymers, preferably glass and polyurethane.
16. Use of the porous membranes of (per)fluorinated amorphous polymers according to ^{claim 1} ~~claims 1-7~~ in separation processes such as ultrafiltration, nanofiltration and as contactor membranes.